

ELECTRICALLY CONDUCTIVE COMPOSITIONS AND METHOD OF MANUFACTURE THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

This application claims benefit to U.S. Provisional Patent Application Serial Number 60/472,618 filed May 22, 2003, which is fully incorporated herein by reference.

BACKGROUND

[0001] This disclosure relates to electrically conductive compositions and methods of manufacture thereof.

[0002] Articles made from polymeric resins are commonly utilized in material-handling and electronic devices such as packaging film, chip carriers, computers, printers and photocopier components where electrostatic dissipation or electromagnetic shielding are important requirements. Electrostatic dissipation (hereinafter ESD) is defined as the transfer of electrostatic charge between bodies at different potentials by direct contact or by an induced electrostatic field. Electromagnetic shielding (hereinafter EM shielding) effectiveness is defined as the ratio (in decibels) of the proportion of an electromagnetic field incident upon the shield that is transmitted through it. As electronic devices become smaller and faster, their sensitivity to electrostatic charges is increased and hence it is generally desirable to utilize polymeric resins that have been modified to provide improved electrostatically dissipative properties. In a similar manner, it is desirable to modify polymeric resins so that they can provide improved electromagnetic shielding while simultaneously retaining some or all of the advantageous mechanical properties of the polymeric resins.

[0003] Conductive fillers such as graphite fibers derived from pitch and polyacrylonitrile having diameters larger than 2 micrometers are often incorporated into polymeric resins to improve the electrical properties and achieve ESD and EM shielding. However, because of the large size of these graphite fibers, the

incorporation of such fibers generally causes a decrease in the mechanical properties such as impact. There accordingly remains a need in the art for conductive polymeric compositions, which while providing adequate ESD and EM shielding, can retain their mechanical properties.

FIGURES

[0004] Figure 1 is a depiction of the various ways in which the graphene sheets can roll up to produce nanotubes of helical structures. The helical structures may be either of the zigzag or the armchair configuration; and

[0005] Figure 2 is a graphical representation depicting reductions in the specific volume resistivity for compositions containing magnesium oxide and titanium oxide when subjected to mixing for different time intervals.

SUMMARY OF THE INVENTION

[0006] An electrically conductive composition comprises a polymeric resin; a nanosized dispersion agent; and carbon nanotubes, wherein the composition has an electrical volume resistivity less than or equal to about 10^8 ohm-cm, and a notched Izod impact strength greater than or equal to about 5 kilojoules/square meter.

[0007] In another embodiment, a method for manufacturing an electrically conductive composition comprises blending a polymeric resin, a nanosized dispersion agent and single wall carbon nanotubes, wherein the composition has an electrical volume resistivity less than or equal to about 10^8 ohm-cm, and a notched Izod impact strength greater than or equal to about 5 kilojoules/square meter.

DETAILED DESCRIPTION OF THE INVENTION

[0008] Disclosed herein are compositions comprising polymeric resins, nanosized dispersion agents and carbon nanotubes that have a bulk volume resistivity less than or equal to about 10^8 ohm-cm, while displaying impact properties greater than or equal to about 5 kilojoules/square meter and a Class A surface finish. The nanosized dispersion agents promote the dispersion of the carbon nanotubes within

the polymeric resin with minimal degradation to the aspect ratio of the carbon nanotubes. This permits the use of smaller amounts of carbon nanotubes in the composition while obtaining levels of electrical conductivity comparable with the use of larger quantities of carbon nanotubes having smaller aspect ratios. The use of smaller amounts of carbon nanotubes allows for the retention of intrinsic properties of the polymeric resin such as ductility, flexibility, impact strength, and the like.

[0009] In one embodiment, the composition has a surface resistivity greater than or equal to about 10^8 ohm/square (ohm/sq) while having a bulk volume resistivity less than or equal to about 10^8 ohm-cm, while displaying impact properties greater than or equal to about 5 kilojoules/square meter and a Class A surface finish. Such compositions can be advantageously utilized in computers, electronic goods, semi-conductor components, circuit boards, or the like which need to be protected from electrostatic dissipation. They may also be used advantageously in automotive body panels both for interior and exterior components of automobiles that can be electrostatically painted if desired.

[0010] The polymeric resin used in the conductive compositions may be selected from a wide variety of thermoplastic resins, blend of thermoplastic resins, or blends of thermoplastic resins with thermosetting resins. The polymeric resin may also be a blend of polymers, copolymers, terpolymers, or combinations comprising at least one of the foregoing polymeric resins. Specific, but non-limiting examples of thermoplastic resins include polyacetals, polyacrylics, polycarbonates, polystyrenes, polyesters, polyamides, polyamideimides, polyarylates, polyurethanes, polyarylsulfones, polyethersulfones, polyarylene sulfides, polyvinyl chlorides, polysulfones, polyetherimides, polytetrafluoroethylenes, polyetherketones, polyether etherketones, and combinations comprising at least one of the foregoing polymeric resins.

[0011] Specific non-limiting examples of blends of thermoplastic resins include acrylonitrile-butadiene-styrene/nylon, polycarbonate/acrylonitrile-butadiene-styrene, polyphenylene ether/polystyrene, polyphenylene ether/polyamide,

polycarbonate/polyester, polyphenylene ether/polyolefin, and combinations comprising at least one of the foregoing blends of thermoplastic resins.

[0012] The polymeric resin is generally used in amounts of about 5 to about 99.999 weight percent (wt%). Within this range, it is generally desirable use the polymeric resin or resinous blend in an amount of greater than or equal to about 10 wt%, preferably greater or equal to about 30 wt%, and more preferably greater than or equal to about 50 wt% of the total weight of the composition. The polymeric resins or resinous blends are furthermore generally used in amounts less than or equal to about 99.99 wt%, preferably less than or equal to about 99.5 wt%, more preferably less than or equal to about 99.3 wt% of the total weight of the composition.

[0013] The carbon nanotubes used in the composition may be single wall carbon nanotubes (SWNTs), multiwall carbon nanotubes (MWNTs) or vapor grown carbon fibers (VGCF). Single wall carbon nanotubes used in the composition may be produced by laser-evaporation of graphite or carbon arc synthesis. These SWNTs generally have a single wall comprising a graphene sheet with outer diameters of about 0.7 to about 2.4 nanometers (nm). SWNTs having aspect ratios of greater than or equal to about 5, preferably greater than or equal to about 100, more preferably greater than or equal to about 1000 are generally utilized in the compositions. While the SWNTs are generally closed structures having hemispherical caps at each end of the respective tubes, it is envisioned that SWNTs having a single open end or both open ends may also be used. The SWNTs generally comprise a central portion, which is hollow, but may be filled with amorphous carbon.

[0014] In one embodiment, the SWNTs may exist in the form of rope-like-aggregates. These aggregates are commonly termed “ropes” and are formed as a result of Van der Waal’s forces between the individual carbon nanotubes. The individual nanotubes in the ropes may slide against one another and rearrange themselves within the rope in order to minimize the free energy. Ropes generally having between 10 and 10^5 nanotubes may be used in the compositions. Within this range it is generally desirable to have ropes having greater than or equal to about 100, preferably greater than or equal to about 500 nanotubes. Also desirable are ropes

having less than or equal to about 10^4 nanotubes, preferably less than or equal to about 5,000 nanotubes. It is generally desirable for the SWNTs to have an inherent thermal conductivity of at least 2000 Watts per meter Kelvin (W/m-K) and an inherent electrical conductivity of 10^4 Siemens/centimeter (S/cm). It is also generally desirable for the SWNTs to have a tensile strength of at least 80 gigapascals (GPa) and a stiffness of at least about 0.5 terapascals (TPa).

[0015] In another embodiment, the SWNTs may comprise a mixture of metallic nanotubes and semi-conducting nanotubes. Metallic nanotubes are those that display electrical characteristics similar to metals, while the semi-conducting nanotubes are those, which are electrically semi-conducting. In general the manner in which the graphene sheet is rolled up produces nanotubes of various helical structures. These structures as well as the lattice vectors is shown in Figure 1. As may be seen from the Figure 1, the integer lattice vectors m and n are added together and the tail and head of the resulting vector are placed on top of each other in the final nanotube structure. Zigzag nanotubes have $(n,0)$ lattice vector values, while armchair nanotubes have (n,n) lattice vector values. Zigzag and armchair nanotubes constitute the two possible achiral conformations, all other (m,n) lattice vector values yield chiral nanotubes. In order to minimize the quantity of SWNTs utilized in the composition, it is generally desirable to have the metallic nanotubes constitute as large a fraction of the total amount of SWNTs used in the composition. It is generally desirable for the SWNTs used in the composition to comprise metallic nanotubes in an amount of greater than or equal to about 1 wt%, preferably greater than or equal to about 20 wt%, more preferably greater than or equal to about 30 wt%, even more preferably greater than or equal to about 50 wt%, and most preferably greater than or equal to about 99.9 wt% of the total weight of the SWNTs. In certain situations it may be is generally desirable for the SWNTs used in the composition to comprise semi-conducting nanotubes in an amount of greater than or equal to about 1 wt%, preferably greater than or equal to about 20 wt%, more preferably greater than or equal to about 30 wt%, even more preferably greater than or equal to about 50 wt%, and most preferably greater than or equal to about 99.9 wt% of the total weight of the SWNTs.

[0016] SWNTs are generally used in amounts of about 0.001 to about 50 wt% of the total weight of the composition when desirable. Within this range, SWNTs are generally used in amounts greater than or equal to about 0.25 wt%, preferably greater or equal to about 0.5 wt%, more preferably greater than or equal to about 1 wt% of the total weight of the composition. SWNTs are furthermore generally used in amounts less than or equal to about 30 wt%, preferably less than or equal to about 10 wt%, more preferably less than or equal to about 5 wt% of the total weight of the composition.

[0017] MWNTs derived from processes such as laser ablation and carbon arc synthesis may also be used in the compositions. MWNTs have at least two graphene layers bound around an inner hollow core. Hemispherical caps generally close both ends of the MWNTs, but it may be desirable to use MWNTs having only one hemispherical cap or MWNTs, which are devoid of both caps. MWNTs generally have diameters of about 2 to about 50 nm. Within this range it is generally desirable to use MWNTs having diameters less than or equal to about 40, preferably less than or equal to about 30, and more preferably less than or equal to about 20 nm. When MWNTs are used it is preferred to have an average aspect ratio greater than or equal to about 5, preferably greater than or equal to about 100, more preferably greater than or equal to about 1000.

[0018] MWNTs are generally used in amounts of about 0.001 to about 50 wt% of the total weight of the composition when desirable. Within this range, MWNTs are generally used in amounts greater than or equal to about 0.25 wt%, preferably greater or equal to about 0.5 wt%, more preferably greater than or equal to about 1 wt% of the total weight of the composition. MWNTs are furthermore generally used in amounts less than or equal to about 30 wt%, preferably less than or equal to about 10 wt%, more preferably less than or equal to about 5 wt% of the total weight of the composition.

[0019] Other conductive fillers such as vapor grown carbon fibers, carbon black, conductive metallic fillers, solid non-metallic, conductive fillers, or the like, or combinations comprising at least one of the foregoing may optionally be used in the

compositions. Vapor grown carbon fibers or small graphitic or partially graphitic carbon fibers, also referred to as vapor grown carbon fibers (VGCF), having diameters of about 3.5 to about 2000 nanometers (nm) and an aspect ratio greater than or equal to about 5 may also be used. When VGCF are used, diameters of about 3.5 to about 500 nm are preferred, with diameters of about 3.5 to about 100 nm being more preferred, and diameters of about 3.5 to about 50 nm most preferred. It is also preferable to have average aspect ratios greater than or equal to about 100 and more preferably greater than or equal to about 1000. Representative VGCF are described in, for example, U.S. Patent Nos. 4,565,684 and 5,024,818 to Tibbetts et al.; 4,572,813 to Arakawa; 4,663,230 and 5,165,909 to Tennent; 4,816,289 to Komatsu et al.; 4,876,078 to Arakawa et al.; 5,589,152 to Tennent et al.; and 5,591,382 to Nahass et al.

[0020] VGCF are generally used in amounts of about 0.001 to about 50 wt% of the total weight of the composition when desirable. Within this range, VGCF are generally used in amounts greater than or equal to about 0.25 wt%, preferably greater or equal to about 0.5 wt%, more preferably greater than or equal to about 1 wt% of the total weight of the composition. VGCF are furthermore generally used in amounts less than or equal to about 30 wt%, preferably less than or equal to about 10 wt%, more preferably less than or equal to about 5 wt% of the total weight of the composition.

[0021] In one embodiment, the carbon nanotubes used in the composition may comprise impurities. Impurities are generally obtained as a result of the catalysts used in the synthesis of the carbon nanotubes as well from other non- carbon nanotube carbonaceous by-products of the synthesis. Catalytic impurities are generally metals such as cobalt, iron, yttrium, cadmium, copper, nickel, oxides of metals such as ferric oxide, aluminum oxide, silicon dioxide, or the like, or combinations comprising at least one of the foregoing impurities. Carbonaceous by-products of the reaction are generally soot, amorphous carbon, coke, multiwall nanotubes or the like, or combinations comprising at least one of the foregoing carbonaceous by-products. In general, the single wall carbon nanotubes may contain metals such as cobalt, iron, yttrium, cadmium, copper, nickel, oxides of metals such as ferric oxide, aluminum

oxide, silicon dioxide, carbonaceous reaction by-products such as soot, amorphous carbon, coke, multiwall nanotubes, or the like, as impurities.

[0022] In general, the carbon nanotubes used in the composition may comprise an amount of about 1 to about 80 wt% impurities. Within this range, the carbon nanotubes may have an impurity content greater than or equal to about 5, preferably greater than or equal to about 7, and more preferably greater than or equal to about 8 wt%, of the total weight of the carbon nanotubes. Also desirable within this range, is an impurity content of less than or equal to about 50, preferably less than or equal to about 45, and more preferably less than or equal to about 40 wt% of the total weight of the carbon nanotubes.

[0023] The carbon nanotubes utilized in the composition may also be derivatized with functional groups to improve compatibility and facilitate the mixing with the polymeric resin. The carbon nanotubes may be functionalized on either the graphene sheet constituting the sidewall, a hemispherical cap or on both the side wall as well as the hemispherical endcap. Functionalized carbon nanotubes having the formula (I)

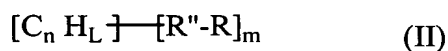


wherein n is an integer, L is a number less than 0.1n, m is a number less than 0.5n, and wherein each of R is the same and is selected from -SO₃H, -NH₂, -OH, -C(OH)R', -CHO, -CN, -C(O)Cl, -C(O)SH, -C(O)OR', -SR', -SiR₃', -Si(OR')_yR'(_{3-y}), -R'', -AlR₂', halide, ethylenically unsaturated functionalities, epoxide functionalities, or the like, wherein y is an integer equal to or less than 3, R' is hydrogen, alkyl, aryl, cycloalkyl, aralkyl, cycloaryl, poly(alkylether), or the like and R'' is fluoroalkyl, fluoroaryl, fluorocycloalkyl, fluoroaralkyl, cycloaryl, or the like. The carbon atoms, C_n, are surface carbons of a carbon nanotube. In both uniformly and non-uniformly substituted carbon nanotubes, the surface atoms C_n are reacted.

[0024] Non-uniformly substituted carbon nanotubes may also be used in the composition. These include compositions of the formula (I) shown above wherein n,

L, m, R and the SWNT itself are as defined above, provided that each of R does not contain oxygen, or, if each of R is an oxygen-containing group, COOH is not present.

[0025] Also included in the invention are functionalized nanotubes having the formula (II)



where n, L, m, R' and R have the same meaning as above. Most carbon atoms in the surface layer of a carbon nanotube are basal plane carbons. Basal plane carbons are relatively inert to chemical attack. At defect sites, where, for example, the graphitic plane fails to extend fully around the carbon nanotube, there are carbon atoms analogous to the edge carbon atoms of a graphite plane. The edge carbons are reactive and must contain some heteroatom or group to satisfy carbon valency.

[0026] The substituted carbon nanotubes described above may advantageously be further functionalized. Such compositions include compositions of the formula (III)



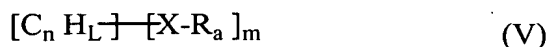
where n, L and m are as described above, A is selected from -OY, -NHY, -CR'₂-OY, -C(O)OY, -C(O)NR'Y, -C(O)SY, or -C(O)Y, wherein Y is an appropriate functional group of a protein, a peptide, an enzyme, an antibody, a nucleotide, an oligonucleotide, an antigen, or an enzyme substrate, enzyme inhibitor or the transition state analog of an enzyme substrate or is selected from -R'OH, -R'NH₂, -R'SH, -R'CHO, -R'CN, -R'X, -R'SiR'₃, -RSi-(OR')_y-R'(_{3-y}), -R'Si-(O-SiR'₂)-OR', -R'-R'', -R'-NCO, (C₂H₄O)_wY, -(C₃H₆O)_wH, -(C₂H₄O)_wR', -(C₃H₆O)_wR' and R'', wherein w is an integer greater than one and less than 200.

[0027] The functional carbon nanotubes of structure (II) may also be functionalized to produce compositions having the formula (IV)



where n, L, m, R' and A are as defined above.

[0028] The compositions of the invention also include carbon nanotubes upon which certain cyclic compounds are adsorbed. These include compositions of matter of the formula (V)



where n is an integer, L is a number less than 0.1n, m is less than 0.5n, a is zero or a number less than 10, X is a polynuclear aromatic, polyheteronuclear aromatic or metallopolyheteronuclear aromatic moiety and R is as recited above. Preferred cyclic compounds are planar macrocycles such as re porphyrins and phthalocyanines.

[0029] The adsorbed cyclic compounds may be functionalized. Such compositions include compounds of the formula (VI)



where m, n, L, a, X and A are as defined above and the carbons are on the SWNT.

[0030] Without being bound to a particular theory, the functionalized carbon nanotubes are better dispersed into polymeric resins because the modified surface properties may render the carbon nanotube more compatible with the polymeric resin, or, because the modified functional groups (particularly hydroxyl or amine groups) are bonded directly to the polymeric resin as terminal groups. In this way, polymeric resins such as polycarbonates, polyamides, polyesters, polyetherimides, or the like, bond directly to the carbon nanotubes, thus making the carbon nanotubes easier to disperse with improved adherence to the polymeric resin.

[0031] Functional groups may generally be introduced onto the outer surface of the carbon nanotubes by contacting the carbon nanotubes with a strong oxidizing agent for a period of time sufficient to oxidize the surface of the carbon nanotubes and further contacting the carbon nanotubes with a reactant suitable for adding a

functional group to the oxidized surface. Preferred oxidizing agents are comprised of a solution of an alkali metal chlorate in a strong acid. Preferred alkali metal chlorates are sodium chlorate or potassium chlorate. A preferred strong acid used is sulfuric acid. Periods of time sufficient for oxidation are about 0.5 hours to about 24 hours.

[0032] Carbon black may also be optionally used, preferred carbon blacks are those having average particle sizes less than about 200 nm, preferably less than about 100 nm, more preferably less than about 50 nm. Preferred conductive carbon blacks may also have surface areas greater than about 200 square meter per gram (m^2/g), preferably greater than about 400 m^2/g , yet more preferably greater than about 1000 m^2/g . Preferred conductive carbon blacks may have a pore volume (dibutyl phthalate absorption) greater than about 40 cubic centimeters per hundred grams ($\text{cm}^3/100\text{g}$), preferably greater than about 100 $\text{cm}^3/100\text{g}$, more preferably greater than about 150 $\text{cm}^3/100\text{g}$. Exemplary carbon blacks include the carbon black commercially available from Columbian Chemicals under the trade name Conductex®; the acetylene black available from Chevron Chemical, under the trade names S.C.F. (Super Conductive Furnace) and E.C.F. (Electric Conductive Furnace); the carbon blacks available from Cabot Corp. under the trade names Vulcan XC72 and Black Pearls; and the carbon blacks commercially available from Akzo Co. Ltd under the trade names Ketjen Black EC 300 and EC 600. Preferred conductive carbon blacks may be used in amounts from about 2 wt% to about 25 wt% based on the total weight of the composition.

[0033] Solid conductive metallic fillers may also optionally be used in the conductive compositions. These may be electrically conductive metals or alloys that do not melt under conditions used in incorporating them into the polymeric resin, and fabricating finished articles therefrom. Metals such as aluminum, copper, magnesium, chromium, tin, nickel, silver, iron, titanium, and mixtures comprising any one of the foregoing metals can be incorporated into the polymeric resin as conductive fillers. Physical mixtures and true alloys such as stainless steels, bronzes, and the like, may also serve as conductive filler particles. In addition, a few intermetallic chemical compounds such as borides, carbides, and the like, of these metals, (e.g., titanium diboride) may also serve as conductive filler particles. Solid

non-metallic, conductive filler particles such as tin-oxide, indium tin oxide, and the like may also optionally be added to render the polymeric resin conductive. The solid metallic and non-metallic conductive fillers may exist in the form of powder, drawn wires, strands, fibers, tubes, nanotubes, flakes, laminates, platelets, ellipsoids, discs, and other commercially available geometries commonly known in the art.

[0034] Non-conductive, non-metallic fillers that have been coated over a substantial portion of their surface with a coherent layer of solid conductive metal may also optionally be used in the conductive compositions. The non-conductive, non-metallic fillers are commonly referred to as substrates, and substrates coated with a layer of solid conductive metal may be referred to as “metal coated fillers”. Typical conductive metals such as aluminum, copper, magnesium, chromium, tin, nickel, silver, iron, titanium, and mixtures comprising any one of the foregoing metals may be used to coat the substrates. Examples of substrates are well known in the art and include those described in “Plastic Additives Handbook, 5th Edition” Hans Zweifel, Ed, Carl Hanser Verlag Publishers, Munich, 2001. Non-limiting examples of such substrates include silica powder, such as fused silica and crystalline silica, boron-nitride powder, boron-silicate powders, alumina, magnesium oxide (or magnesia), wollastonite, including surface-treated wollastonite, calcium sulfate (as its anhydride, dihydrate or trihydrate), calcium carbonate, including chalk, limestone, marble and synthetic, precipitated calcium carbonates, generally in the form of a ground particulates, talc, including fibrous, modular, needle shaped, and lamellar talc, glass spheres, both hollow and solid, kaolin, including hard, soft, calcined kaolin, and kaolin comprising various coatings known in the art to facilitate compatibility with the polymeric matrix resin, mica, feldspar, silicate spheres, flue dust, cenospheres, fillite, aluminosilicate (armospheres), natural silica sand, quartz, quartzite, perlite, tripoli, diatomaceous earth, synthetic silica, and mixtures comprising any one of the foregoing. All of the above substrates may be coated with a layer of metallic material for use in the conductive compositions.

[0035] Regardless of the exact size, shape and composition of the solid metallic and non-metallic conductive filler particles, they may be dispersed into the polymeric resin at loadings of about 0.001 to about 50 wt% of the total weight of the

composition when desired. Within this range it is generally desirable to have the solid metallic and non-metallic conductive filler particles in an amount of greater than or equal to about 1 wt%, preferably greater than or equal to about 1.5 wt% and more preferably greater than or equal to about 2 wt% of the total weight of the composition. The loadings of said solid metallic and non-metallic conductive filler particles may be less than or equal to 40 wt%, preferably less than or equal to about 30 wt%, more preferably less than or equal to about 25 wt% of the total weight of the composition.

[0036] Nanosized dispersion agents are generally used in the composition in order to facilitate the dispersion of the carbon nanotubes in the polymeric resin. The nanosized dispersion agents are electrically non-conducting. The nanosized dispersion agents are generally ceramic particles such as metal oxides, highly crosslinked silicones, polyhedral oligomeric silsesquioxanes (POSS) macromers, metal carbides, nanoclays and the like, which have maximum particle sizes less than or equal to about 1200 nm. In general it is desirable to use nanosized dispersion agents wherein the particle sizes are less than or equal to about 500, preferably less than or equal to about 200, preferably less than or equal to about 100, and more preferably less than or equal to about 40 nanometers. In general, it is desirable to have at least 90 wt% of the nanosized dispersion agents having a particle size less than or equal to 500 nm, at least 80 wt% less than or equal to about 200 nm and more preferably at least 50 wt% less than or equal to about 100 nm.

[0037] The nanosized dispersion particles may have either smooth or rough surfaces. In one embodiment, it is generally desirable for the nanosized particles to have smooth surfaces in order to behave as molecular ball bearings. Without being limited by theory, it is believed that the molecular ball bearings facilitate the dispersion of the carbon nanotubes by inserting themselves between the carbon nanotubes and allowing the nanotubes to slide apart.

[0038] Nanosized metal oxides that may be used in the compositions are metal oxides of alkali earth metals, alkaline earth metals, transition metals and other commonly used metals. Suitable examples of metal oxides are calcium oxide, cerium oxide, magnesium oxide, titanium oxide, zinc oxide, silicon oxide, copper oxide,

aluminum oxide, or the like, or combinations comprising at least one of the foregoing metal oxides. Nanosized metal carbides such as silicon carbide, titanium carbide, tungsten carbide, iron carbide, or the like, or combinations comprising at least one of the foregoing metal carbides may also be used in the compositions. The metal oxides and carbides are generally particles having surface areas in an amount of about 1 to about 1000 m²/gm. Within this range it is generally desirable for the metal oxides and carbides to have surface areas greater than or equal to about 5 square meter/gram (m²/gm), preferably greater than or equal to about 10 m²/gm, and more preferably greater than or equal to about 15 m²/gm. Also desirable within this range is a surface area less than or equal to about 950 m²/gm, preferably less than or equal to about 900 m²/gm, and more preferably less than or equal to about 875 m²/gm.

[0039] It is generally desirable for the nanosized metal oxide and carbide particles to have bulk densities in an amount of about 0.2 to about 2.5 grams per cubic centimeter; true densities in an amount of about 3 to about 7 grams per cubic centimeter and an average pore diameter of about 10 to about 250 angstroms.

[0040] Commercially available examples of nanosized metal oxides are NANOACTIVETM calcium oxide, NANOACTIVETM calcium oxide plus, NANOACTIVETM cerium oxide, NANOACTIVETM magnesium oxide, NANOACTIVETM magnesium oxide plus, NANOACTIVETM titanium oxide, NANOACTIVETM zinc oxide, NANOACTIVETM silicon oxide, NANOACTIVETM copper oxide, NANOACTIVETM aluminum oxide, NANOACTIVETM aluminum oxide plus, all commercially available from NanoScale Materials Incorporated. Commercially available examples of nanosized metal carbides are titanium carbonitride, silicon carbide, silicon carbide-silicon nitride, and tungsten carbide all commercially available from Pred Materials International Incorporated.

[0041] Nanoclays (nanosized clays) may also be used in the compositions to facilitate the dispersion of the carbon nanotubes. Nanoclays are generally plate-like materials, the clay mineral being generally selected from smectite, vermiculite and halloysite clays. The smectite clay in turn can be selected from montmorillonite, saponite, beidellite, nontrite, hectorite or the like, or combinations comprising at least

one of the foregoing clays. A preferred clay mineral is the montmorillonite clay, a layered aluminosilicate. The nanoclay platelets generally have a thickness of about 3 to about 3000 angstroms and a size in the planar direction ranging of about 0.01 micron to about 100 micrometers. The aspect ratio of the nanoclays is generally of the order of about 10 to about 10,000. The respective clay platelets are separated by a gallery, i.e., a space between parallel layers of clay platelets containing various ions holding the platelets together. One such material is CLOISITE®10A commercially available from Southern Clay Products, its platelets having a thickness of about 0.001 micrometers (10 angstroms) and a size in the planar direction of about 0.15 to about 0.20 micrometers.

[0042] Swellable nanoclays may also be used in the compositions to disperse carbon nanotubes. Useful swellable layered materials include phyllosilicates. Examples of such materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadiite, kenyaite, vermiculite, or the like of combinations comprising at least one of the foregoing swellable nanoclays. Other useful layered materials include illite minerals such as ledikite and admixtures of illites with the clay minerals named above.

[0043] POSS of the generic formula $(R\text{SiO}_{1.5})_n$, wherein R is a hydrocarbon and n is 6, 8, 10, 12, or higher may also be used in the compositions. These molecules have rigid, thermally stable silicon-oxygen frameworks with an oxygen to silicon ratio of 1.5, and covalently-bound hydrocarbon groups that provide an organic outer layer comprising, for example, phenyl, isooctyl, cyclohexyl, cyclopentyl, isobutyl, or other groups. Such silsesquioxanes include, for example, dodecaphenyl-POSS, octaisooctyl-POSS, octacyclohexyl-POSS, octacyclopentyl-POSS, octaisobutyl-POSS and the like. POSS typically have surface areas greater than 400 square meters per gram (m^2/gm).

[0044] Highly crosslinked silicone nanosized agents having smooth surfaces may also behave as molecular ball bearings and thereby facilitate the dispersion of the carbon nanotubes. These nanosized agents are generally monodispersed in size and are derived from the hydrolysis and condensation of alkyl alkoxy-silanes. These

silicon nanosized agents are generally intermediate between inorganic and organic particles and have a 3-dimensional network structure. Without being limited by theory, it is believed that the molecular ball bearings when lodged in the interstices of a carbon nanotube agglomerate or cluster can facilitate a lowering of the friction between the carbon nanotubes and thus reduce the stresses used in disentangling and dispersion of the nanotubes. Suitable examples of highly crosslinked silicone nanosized agents are TOSPEARL[®] particles manufactured by GE Silicones. TOSPEARL[®] particles display good hot slip properties, good anti-block properties and have a low influence on optical properties. These TOSPEARL[®] nanosized particles generally have an average size of about 300 nm to about 1500 nm. Within this range, it is generally desirable to have an average particle size of greater than or equal to about 400 and preferably greater than or equal to about 500 nm. Also desirable within this range is an average particle size of less than or equal to about 1100 nm and more preferably less than or equal to about 800 nm.

[0045] It is generally desirable to add the nanosized dispersion agents in amounts of about 0.01 to about 20 wt% based on the total weight of the composition. Within this range it is generally desirable to use the nanosized dispersion agents in amounts of greater than or equal to about 0.5, preferably greater than or equal to about 0.7, and more preferably greater than or equal to about 1.0 wt% based on the total weight of the composition. Also desirable is an amount of less than or equal to about 15, preferably less than or equal to about 10, and more preferably less than or equal to about 5 wt% based on the total weight of the composition.

[0046] Nanosized dispersion agents may also be used in the compositions in masterbatch form if desired. As defined herein, as masterbatch is generally a composition comprising the nanosized dispersion agent and a binder. The binder may be a polymer, homopolymer, monomer, or any other material that may suitably bind the nanosized dispersion agent such that it may be formed into a desired usable shape such as a pellet, strand, briquette, sheet, block, brick, or the like. When a nanosized dispersion agent is used in masterbatch form, the nanosized dispersion agent may be present in the masterbatch in an amount of about 1 to about 50 wt%. Within this range, it is generally desirable to use nanosized dispersion agents in an amount of

greater than or equal to about 1.5 wt%, preferably greater or equal to about 2wt%, more preferably greater than or equal to about 2.5 wt% of the total weight of the masterbatch. Also desirable are nanosized dispersion agents in an amount of less than or equal to about 30 wt%, preferably less than or equal to about 10 wt%, more preferably less than or equal to about 5 wt% of the total weight of the masterbatch. It may also be desirable to use a masterbatch comprising both carbon nanotubes and the nanosized dispersing agents.

[0047] The polymeric resin together with the nanosized dispersion agents, carbon nanotubes and any other optionally desired conductive fillers such as the carbon black, solid metallic and non-metallic conductive filler particles may generally be processed in several different ways such as, but not limited to melt blending, solution blending, or the like, or combinations comprising at least one of the foregoing methods of blending. Melt blending of the composition involves the use of shear force, extensional force, compressive force, ultrasonic energy, electromagnetic energy, thermal energy or combinations comprising at least one of the foregoing forces or forms of energy and is conducted in processing equipment wherein the aforementioned forces are exerted by a single screw, multiple screws, intermeshing co-rotating or counter rotating screws, non-intermeshing co-rotating or counter rotating screws, reciprocating screws, screws with pins, screws with screens, barrels with pins, rolls, rams, helical rotors, or combinations comprising at least one of the foregoing.

[0048] Melt blending involving the aforementioned forces may be conducted in machines such as, but not limited to single or multiple screw extruders, Buss kneader, Henschel, helicones, Ross mixer, Banbury, roll mills, molding machines such as injection molding machines, vacuum forming machines, blow molding machine, or then like, or combinations comprising at least one of the foregoing machines.

[0049] In one embodiment, the polymeric resin in powder form, pellet form, sheet form, or the like, may be first dry blended with the nanosized dispersion agents, carbon nanotubes and other optional fillers if desired in a Henschel or a roll mill, prior

to being fed into a melt blending device such as an extruder or Buss kneader. While it is generally desirable for the shear forces in the melt blending device to generally cause a dispersion of the carbon nanotubes and /or the nanosized dispersion agents in the polymeric resin, it is also desired to preserve the aspect ratio of the carbon nanotubes during the melt blending process. In order to do so, it may be desirable to introduce the carbon nanotubes into the melt blending device in the form of a masterbatch. In such a process, the masterbatch may be introduced into the melt blending device downstream of the polymeric resin. As stated above, the nanosized dispersion agents may also be added to the composition in the form of a masterbatch if desired or alternatively, a masterbatch comprising both the carbon nanotubes and the nanosized dispersion agents may be used if desired.

[0050] A melt blend is one where at least a portion of the polymeric resin has reached a temperature greater than or equal to about the melting temperature, if the resin is a semi-crystalline polymeric resin, or the flow point (e.g., the glass transition temperature) if the resin is an amorphous resin during the blending process. A dry blend is one where the entire mass of polymeric resin is at a temperature less than or equal to about the melting temperature if the resin is a semi-crystalline polymeric resin, or at a temperature less than or equal to the flow point if the polymeric resin is an amorphous resin and wherein polymeric resin is substantially free of any liquid-like fluid during the blending process. A solution blend, as defined herein, is one where the polymeric resin is suspended in a liquid-like fluid such as, for example, a solvent or a non-solvent during the blending process.

[0051] When a masterbatch is used, the carbon nanotubes may be present in the masterbatch in an amount of about 1 to about 50 wt%. Within this range, it is generally desirable to use carbon nanotubes in an amount of greater than or equal to about 1.5 wt%, preferably greater or equal to about 2wt%, more preferably greater than or equal to about 2.5 wt% of the total weight of the masterbatch. Also desirable are carbon nanotubes in an amount of less than or equal to about 30 wt%, preferably less than or equal to about 10 wt%, more preferably less than or equal to about 5 wt% of the total weight of the masterbatch. In one embodiment pertaining to the use of masterbatches, while the masterbatch containing the carbon nanotubes may not have a

measurable bulk or surface resistivity either when extruded in the form of a strand or molded into the form of dogbone, the resulting composition into which the masterbatch is incorporated has a measurable bulk or surface resistivity, even though the weight fraction of the carbon nanotubes in the composition is lower than that in the masterbatch. It is preferable for the polymeric resin in such a masterbatch to be semi-crystalline. Examples of semi-crystalline polymeric resins which display these characteristics and which may be used in masterbatches are polypropylene, polyamides, polyesters, or the like, or combinations comprising at least one of the foregoing semi-crystalline polymeric resins.

[0052] In another embodiment relating to the use of masterbatches in the manufacture of the composition, it is sometimes desirable to have the masterbatch comprising a polymeric resin that is the same as the polymeric resin that forms the continuous phase of the composition. This feature permits the use of substantially smaller proportions of the SWNTs, since only the continuous phase carries the SWNTs that provide the composition with the requisite volume and surface resistivity. In yet another embodiment relating to the use of masterbatches in polymeric blends, it may be desirable to have the masterbatch comprising a polymeric resin that is different in chemistry from other the polymeric that are used in the composition. In this case, the polymeric resin of the masterbatch will form the continuous phase in the blend.

[0053] The composition comprising the polymeric resin, nanosized dispersion aids and the carbon nanotubes may be subject to multiple blending and forming steps if desirable. For example, the composition may first be extruded and formed into pellets. The pellets may then be fed into a molding machine where it may be formed into other desirable shapes such as housing for computers, automotive panels that can be electrostatically painted, or the like. Alternatively, the composition emanating from a single melt blender may be formed into sheets or strands and subjected to post-extrusion processes such as annealing, uniaxial or biaxial orientation.

[0054] In one embodiment involving the use of post-processing, the melt blended composition is further subjected to ultradrawing in the uniaxial direction

utilizing draw ratios of about 2 to about 1,000,000. The high ultradraw ratios generally facilitates the formation of shish-kebab semi-crystalline structures, which may contain carbon nanotubes in the amorphous regions. In another embodiment, the composition is further stressed uniaxially or biaxially to produce a film having a thickness of about 0.01 micrometers to about 5000 micrometers. If the film comprises a semi-crystalline polymeric resin, it is generally desirable for the oriented film to have crystals oriented in the azimuthal direction of about $\theta = 0$ degrees to about $\theta = 80$ degrees. In yet another embodiment related to post-processing after melt blending, the composition is supercooled to a temperature of about 1°C to about 100°C below the melting point after the blending for a time period of about 2 minutes to about 2 hours. The supercooled compositions may generally have macroscopic semi-crystalline structures such as spherulites, which comprise carbon nanotubes.

[0055] In semi-crystalline polymers, the carbon nanotubes may behave as nucleating agents. In order to improve the strength of the composition, it may be desirable to have the crystallites nucleate on the carbon nanotubes. In general it is desirable to have at least 1 wt%, preferably at least 10 wt%, and more preferably at least 15 wt% of the crystallites nucleate on the carbon nanotubes.

[0056] Solution blending may also be used to manufacture the composition. The solution blending may also use additional energy such as shear, compression, ultrasonic vibration, or the like to promote homogenization of the carbon nanotubes and the nanosized dispersion agent with the polymeric resin. In one embodiment, a polymeric resin suspended in a fluid may be introduced into an ultrasonic sonicator along with the carbon nanotubes and/or the nanosized dispersion agents. The mixture may be solution blended by sonication for a time period effective to disperse the carbon nanotubes and/or the nanosized dispersion agents onto the polymeric resin particles. The polymeric resin along with the carbon nanotubes may then be dried, extruded and molded if desired. It is generally desirable for the fluid to swell the polymeric resin during the process of sonication. Swelling the polymeric resin generally improves the ability of the carbon nanotubes to impregnate the polymeric resin during the solution blending process and consequently improves dispersion.

[0057] In another embodiment related to solution blending, the carbon nanotubes and/or the nanosized dispersion agents are sonicated together with polymeric resin precursors. Polymeric resin precursors are generally monomers, dimers, trimers, or the like, which can be reacted into polymeric resins. A fluid such as a solvent may optionally be introduced into the sonicator with the carbon nanotubes and/or the nanosized dispersion agents and the polymeric resin precursor. The time period for the sonication is generally an amount effective to promote encapsulation of the carbon nanotubes and /or the nanosized dispersion agents by the polymeric resin precursor. After the encapsulation, the polymeric resin precursor is then polymerized to form a polymeric resin within which is dispersed the carbon nanotubes and/or the nanosized dispersion agents. This method of dispersion of the carbon nanotubes and/or the nanosized dispersion agents in the polymeric resin promotes the preservation of the aspect ratios of the carbon nanotubes and/or the nanosized dispersion agents, which therefore permits the composition to develop electrical conductivity at lower loading of the carbon nanotubes and /or the nanosized dispersion agents.

[0058] Suitable examples of monomers that may be used to facilitate this method of encapsulation and dispersion are those used in the synthesis of thermoplastic resins such as, but not limited to polyacetals, polyacrylics, polycarbonates, polystyrenes, polyesters, polyamides, polyamideimides, polyarylates, polyurethanes, polyarylsulfones, polyethersulfones, polyarylene sulfides, polyvinyl chlorides, polysulfones, polyetherimides, polytetrafluoroethylenes, polyetherketones, polyether etherketones, or the like. In general, it is desirable to sonicate the mixture of polymeric resin, polymeric resin precursor, fluid and/or the carbon nanotubes and /or the nanosized dispersion agents for a period of about 1 minute to about 24 hours. Within this range, it is desirable to sonicate the mixture for a period of greater than or equal to about 5 minutes, preferably greater than or equal to about 10 minutes and more preferably greater than or equal to about 15 minutes. Also desirable within this range is a time period of less than or equal to about 15 hours, preferably less than or equal to about 10 hours, and more preferably less than or equal to about 5 hours.

[0059] The compositions described above may be used in a wide variety of commercial applications. They may be advantageously utilized as films for packaging electronic components such as computers, electronic goods, semiconductor components, circuit boards, or the like which need to be protected from electrostatic dissipation. They may also be used internally inside computers and other electronic goods to provide electromagnetic shielding to personnel and other electronics located outside the computer as well as to protect internal computer components from other external electromagnetic interference. They may also be used advantageously in automotive body panels both for interior and exterior components of automobiles that can be electrostatically painted if desired.

[0060] The following examples, which are meant to be exemplary, not limiting, illustrate compositions and methods of manufacturing of some of the various embodiments of the electrically conductive compositions described herein.

EXAMPLE 1

[0061] This experiment was undertaken to demonstrate effectiveness of the nanosized dispersing agents in facilitating the dispersion of carbon nanotubes in a polycarbonate resin. In this example, various nanosized dispersion aids listed in Table 1 were mixed with polycarbonate powder and 1 wt% of single wall carbon nanotubes obtained from Carbon Nanotechnologies Incorporated. The polycarbonate powder, the carbon nanotubes and the nanosized dispersion agents were dry blended together in a glass weighing dish and extruded through a DACA mini-extruder to form a strand. The DACA mini twin screw extruder has a maximum mixing volume of 5 cubic centimeters and has a screw speed of from about 10 to about 360 rpm which is digitally controllable in 1 rpm increments. The strands from the extruder were used to make conductivity measurements. The strands were fractured under liquid nitrogen to ensure a clean break, the ends were painted with a silver conductive paint, and the resistance was measured with a Fluke multimeter.

Table 1

Sample #	Nanosized Dispersion Agent	Manufacturer	Wt%
1	Aluminum Oxide	NanoActive	1
2	Magnesium Oxide	NanoActive	1
3	Copper Oxide	NanoActive	1
4	Zinc Oxide	NanoActive	1
5	Calcium Oxide	NanoActive	1
6	Titanium (IV) Oxide (TiO ₂)	NanoActive	1
7	Nanoclays	Nanocor	1
8	Nanosil (SiO ₂)	US Global Aerospace	1
9	Titanium oxide (TiO ₂) (regular)	DuPont	1

[0062] Specific volume resistivity was measured on at least five samples for each composition. While the nanosized particles of aluminum oxide, copper oxide, zinc oxide, calcium oxide and the nanoclays produced no changes in the measured volume resistivity, Figure 2 shows reductions in the specific volume resistivity for samples containing magnesium oxide and titanium oxide when subjected to mixing for different time intervals. The figure details the specific volume resistivity versus the time of mixing for polycarbonate samples containing only 1 wt% carbon nanotubes. The figure also details the specific volume resistivity for samples containing polycarbonate and having 1 wt% carbon nanotubes as well either 1 wt% of nanosized magnesium oxide (MgO) as well as 2 wt% nanosized titanium dioxide (TiO₂). All weight percents are based on the total composition. From the figure it may be seen that for the sample containing only the single wall carbon nanotubes and no nanosized dispersion agent, the specific volume resistivity increases with mixing time. Without being limited by theory, it is believed that the increase in resistivity is due to a decrease in the aspect ratio of the carbon nanotubes as a result of the shear forces in the extruder. The samples having the dispersion agent on the other hand, show a fairly consistent and constant volume resistivity with increased mixing time.

EXAMPLE 2

[0063] This example was conducted to demonstrate the effect of nanosized dispersion agents versus chemically similar agents, which are not nanosized. The non-nanosized agents are called regular agents. The composition for all samples was polycarbonate containing 1 wt% single wall carbon nanotubes and the dispersion agents as shown in Table 2. Table 2 also shows the specific resistivity results for polycarbonate samples having 1 wt% single wall carbon nanotubes and containing either 1 wt% nanosized magnesium oxide or 1 wt% regular magnesium oxide. Resistivity results are also shown for polycarbonate samples having 1 wt% carbon nanotubes containing 2 wt% nanosized titanium dioxide and 2 wt% regular titanium dioxide. The regular titanium dioxide is R10315 commercially available from DuPont having particle size of about 5 micrometers. The individual particles generally agglomerate into clusters having sizes of about 30 to about 150 micrometers and these agglomerates can only be broken down by the application of shear such as, for example, in an extruder.

Table 2

Time of mixing	SVR (ohm-cm) at 1 wt% SWNT	SVR (ohm-cm) at 1 wt% SWNT + 1 wt% nanosized MgO	SVR (ohm-cm) at 1 wt% SWNT + 1 wt% regular MgO	SVR (ohm-cm) at 1 wt% SWNT + 1 wt% nanosized TiO ₂	SVR (ohm-cm) at 1 wt% SWNT + 2 wt% regular TiO ₂
1	7353	---	---	---	---
3	6550	7861	---	8742	---
5	37918	4322	---	5077	---
7	70782	5492	---	6157	---
10	91215	2195	---	4682	---

[0064] From the table it can be seen that the nanosized particles reduce the volume resistivity dramatically, while the regular sized particles have a detrimental effect on the volume resistivity, i.e., there is no measurable conductivity for these samples.

[0065] What is claimed is: